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# ICP-AES Determination of 15 Kind of impurity elements in the Vanadium-aluminum alloy

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**Abstract**

In order to solve the current lack of detection method of impurity elements in the vanadium-aluminum alloy, this paper established by inductively coupled plasma atomic emission spectrometry (ICP-AES) direct simultaneous determination of 15 kind of micro or trace impurity elements, including boron, tungsten, silicon, iron, lead, tin, arsenic, nickel, chromium, cobalt, copper, phosphorus, manganese, magnesium, molybdenum. Vanadium-aluminum alloy sample was digested as the solution with hydrochloric acid and nitric acid, and then by nebulizer spray aerosol was introduced in the plasma torch, the elements in the 8000-10000K high temperature was excited and emission of characteristic lines, by detecting the signal intensity of the characteristic lines for quantitative analysis. Method detailed study between the sample substrate the vanadium and aluminum as well as the co-existing elements disturbing effect, and through the optimal analysis spectral line and the background adjusted the position to avoid the spectrum disturbance. Selects the method which the substrate match and the synchronized background adjust unify to eliminate highly concentrated the vanadium aluminum base body to the test solution atomization, transmission, ICP balanced and the stimulation and the element determination each kind of disturbing effect factor, and optimize the operation control parameters of the spectrometer. In this law determination aerospace rank's vanadium-aluminium alloy impurity element's result indicated: detection limit 5.0 ~ 100μg / L, the background equivalent concentration of 5-95μg / L; recovery rate of 95.3% to 110.0%; in content ≥0.010% RSD≤4.88%; between 0.001% and 0.010% content scope RSD≤8.89%. The actual sample results were the same as the Germany GfE company which is the world-class manufacturer of the vanadium-aluminium alloy, and detection elements and scope over the Gfe. Method measured the European standard samples of the vanadium-iron alloy consistent with the standard value, whose matrix composition similar to the vanadium-aluminium alloy.



*Keywords:*ICP-AES; Vanadium-Aluminum alloy; B; W; Si; Fe; Pb; Sn; As; Ni; Cr; Co; Cu; P; Mn; Mg; Mo;

## 1. Main text

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Vanadium-aluminium alloy has been widely applied in the aerospace, aviation, shipbuilding and other needs high temperature, corrosion resistance, high specific strength of the military and civilian industry. Leading by large commercial aircraft project in China, people pay more attention to and promote research and production of aerospace-grade vanadium aluminium alloy new materials. Vanadium-aluminium alloy testing methods currently little has been report in China, although there have been reported in the literature using ICP-AES detection micro impurity elements silicon, manganese, iron and phosphate in the vanadium-aluminium alloy [1], which can meet the control targets inspection requirements in Chinese national standard GB5063-85 of primary vanadium-aluminium alloy on the silicon ≤ 0.30, Fe ≤ 0.30, etc. Abroad have been reported using bismuth hydroxide precipitation / ICP-AES determination of vanadium-vanadium alloy of eight trace elements copper and cobalt, iron, magnesium, manganese, nickel, titanium, zirconium [2]. But, technical standards of the vanadium-aluminium alloy developed by the world's top manufacturers in Germany GfE company, asking to detect and control requirements of more than 12 impurity elements, such as boron ≤ 0.003, tungsten and molybdenum ≤ 0.015, silicon ≤ 0.35, iron ≤ 0.40, chromium and lead ≤ 0.10, nickel, copper and manganese ≤ 0.05, phosphorus ≤ 0.03, magnesium ≤ 0.25, all of the methods can't meet it. This article does not conduct pre-separation and enrichment, both directly by ICP-AES detection vanadium-aluminium alloy of 15 kind of trace impurity elements of boron, tungsten, silicon, iron, phosphorus, lead, tin, arsenic, nickel, chromium, cobalt, copper, manganese, magnesium and the molybdenum. The method actually was used for determination of vanadium-aluminium alloy sample results were consistent with the German GfE company, again detection of European standard sample to vanadium iron alloy are also consistent with the standard value.

## 2. Experimental

### *2.1. Instruments and reagents*

- iCAP6300 type the full spectrum of direct-reading plasma atomic emission spectrometer (Thermo Fisher U.S. company). Elix water purifier (Millipore Corporation U.S.).
- Excellent level of pure HCl and $HNO_3$. High-purity vanadium powder and aluminum powder (> 99.999%).
- Spectrum of pure or high purity $SiO_2$, $MnO_2$, $KH_2PO_4$, $H_3BO_3$, $MoO_3$, Cu, Co, W, Fe, Sn, $K_2Cr_2O_7$, Ni, $As_2O_5$, Pb, MgO were prepared into a concentration 1mg / mL standard stock solution.

### *2.2. ICP spectrometer operating parameters*

RF power 1150 W, auxiliary gas flow rate (Ar) 1.0 L / min, nebulizer pressure of 0.22 MPa, peristaltic pump speed 55 r / min, observation height 11.2mm, measured integration time 15 s (wavelength greater than 260 nm) or 20 s (wavelength less than 260 nm).

### *2.3. Test Method*

Weigh 0.5 000g vanadium-aluminum alloy sample in a 250 mL Erlenmeyer flask with about 10 mL of water rinse the bottle wall and scattered samples, then add 10 mL HCl, placed in the electric panel heating for digestion reaction. When the sample is dissolved in most, then add 5 mL HNO3 solution, continue to digestion reaction until the sample is dissolved completely. Finally, volume of test solution diluted with water to 100mL volumetric flask.

### *2.4. Calibration curve*

In accordance with 50 vanadium-aluminum alloy (V = 50%, Al = 50%) or 80 vanadium-aluminum alloy (V = 80%, Al = 20%) of the ratio between the weighed high-purity vanadium and aluminum powder, to 1.3 test method, digestion in accordance with 1.3 Test method, and from solution as a blank matrix

matching calibration and rendering solution. Then by adding the element standard solution, prepared with a series of calibration curve concentration gradient, and matrix matching consistent with the sample solution. Used for determination of 50 or 80 type vanadium-vanadium alloy sample.

## 3. Results and discussion

### *3.1. Spectral interference experiments*

ICP-AES is a multi-element analysis method, the basic principle is: Sample is dissolved into solution and is sprayed into aerosol by nebulizer, and then was introduced in the plasma torch. In the plasma of high temperature, the solution evaporation, dissociation, atomization, ionization and excitation, as the excited states of atoms or ions unstable, the outer electrons from the excited state transition back to a lower energy level, at the same time emitting characteristic lines. After all the characteristic lines of separation was splitting system were detected, by the characteristic lines of the analytical wavelength qualitative analysis, based on detection of the intensity of characteristic lines for quantitative analysis. So, in order to avoid the main elements of the matrix vanadium, aluminum and coexistence between the spectral components of interference impact on the determination of elements [1-6], the spectral interference experiment are summarized as follows:

#### *3.1.1. Vanadium and aluminum does not interference with most of the spectral lines*

Vanadium and aluminum does not produce peak in the test line scan window, the blank baseline signals of vanadium and aluminum body was straight, and overlap with pure reagent blank signal baseline, no spectral or background interference. Very few lines cause higher background signal due to peak intensity increased slightly, but the background is smooth straight, using the matrix matching and synchronization of background correction can eliminate background effects, By subtracting the background signal from the peak signal can make the net peak intensity is not affected. Such as: As 189.042nm, B 208.957nm, Fe 240.488nm, Mo 203.844nm, Ni 231.604nm, P 178.284nm, Pb 220.353nm, W 207.911nm.

#### *3.1.2. Although vanadium and aluminum have an impact on some the analytical line, can still be used*

Although exist the vanadium or aluminum interference peak next to the test line, but clearly visible in the spectrum, vanadium or aluminum of interference peaks completely separated with analysis peaks, regional integration in the measured peak there is no overlap between the two. So, if you choose to avoid the background correction point of vanadium, aluminum next to the peak location, you can eliminate their effects. Such as: B 208.893nm by Al 208.916nm, Co 237.862nm by Al 237.840nm, Co 238.892nm by V 238.892nm, Si 221.617 by V 221.603nm the next peak interference, but to eliminate its impact on the determination.

#### *3.1.3. A few lines of vanadium or aluminum serious interference, can not be used*

A few lines by the high intensity matrix elements of vanadium and aluminum serious spectral interference，detection points in the analysis of spectral lines within the region, vanadium, aluminum interference peaks completely overlap with the analytical peaks, can not tell, the result is the determination of vanadium, aluminum interference peak and the sum of the analytical peak signal intensity, this part of the spectrum in this way can not line for analysis. Such as: Si 251.611nm and 212.412nm respectively, by V 251.612nm and 212.411nm, Mn 279.482nm and 294.920nm respectively, by V 279.483nm and 294.917nm, Mo 281.615nm by Al 281.619nm, As 193.759nm by V 193.744nm, Mg 280.270 nm by V 280.280nm, W 209.860nm by Al 209.874nm, W 209.475nm respectively by V 209.466nm and Al 209.474nm double interference and Sn 283.999nm respectively by V 284.011nm and

Al 284.01nm double interference.

*3.1.4. Spectral interferences between impurities is very weak*

Because the vanadium-aluminum alloy contains many components of complex co-existence impurities such as silicon, iron and some other elements, and the spectral interference between coexisting elements can not be ignored. However, interference intensity was low by most co-existence impurities, and the two peaks was clear separation within the detection points region without overlap, It can eliminate the effects as long as the background correction location to avoid interference peak, therefore I can choose for analysis of spectral lines. Such as: Ni 221.647 by Si 221.667nm, P 213.618nm by Cu 213.598nm, Co 238.892nm by Fe 238.863nm the next peak effect.

*3.1.5. There are very few overlapping lines of impurities exist, it can not be used*

Measuring peak and interference peaks overlap completely, can not serve as analysis line, and 261.41 as Pb261.418nm by Fe261.382nm severe spectral interference.

According to the interference with test results, optimization of the analysis wavelength and background correction position, and test the actual analysis of resolution, the results shown in Table 1.

Table 1.The element analysis wavelength, the background correction the position and the Resolution

| Element | Wavelength(nm) | Left background(pixel) | Right background(pixel) | Range of integration(pixel) | Resolution |
|---|---|---|---|---|---|
| As | 189.042 | 2 | 10 | 6 | 0.0072 |
| B | 208.959 | 1 | 11 | 5 | 0.010 |
| Co | 228.616 | 1 | 11 | 6 | 0.0086 |
| Cr | 267.716 | 2 | 10 | 6 | 0.0092 |
| Cu | 224.700 | 1 | 11 | 7 | 0.010 |
| Fe | 240.488 | 2 | 10 | 6 | 0.011 |
| Mg | 279.553 | 1 | 11 | 7 | 0.010 |
| Mn | 293.306 | 3 | 10 | 6 | 0.010 |
| Mo | 203.844 | 1 | 11 | 6 | 0.0085 |
| Ni | 231.604 | 1 | 11 | 6 | 0.0080 |
| P | 178.284 | 2 | 10 | 6 | 0.0064 |
| Pb | 220.353 | 2 | 10 | 6 | 0.0086 |
| Sn | 189.989 | 2 | 10 | 6 | 0.0064 |
| Si | 221.667 | 1 | 10 | 6 | 0.0083 |
| W | 207.911 | 1 | 11 | 6 | 0.0082 |

*3.2. Method detection limits and background equivalent concentration test*

Vanadium, aluminum concentration fluctuations in about 20% without a significant impact on the determination of elements, so as to eliminate matrix effects and other effects, the calibration curve only roughly within a certain range for vanadium, aluminum body match, ensure that calibration curve with the sample solution matrix composition basically the same. According to V = 50% and Al = 50% and V = 80% and Al = 20% weighed high purity vanadium metal powder and aluminum powder, digested into the matrix blank solution in accordance with test method 1.3,and then was measured to calculate the concentration background equivalent concentration, and parallel and continuous determination of 11 times, three times the standard deviation of the elements as the method detection limit, the standard deviation calculated by the formula $S = \sqrt{\frac{\sum (x_i - \bar{x})^2}{n-1}}$. Shown in Table 2.

Table 2.The method background equivalent density and the element Detection limit (n=11, k=3) (%)

| Elemen | BEC | Detection limits | Element | BEC | Detection limits | Element | BEC | Detection limits |
|---|---|---|---|---|---|---|---|---|
| As | 0.0011 | 0.0011 | Mo | 0.0001 | 0.0002 | Mg | 0.0009 | 0.0001 |
| B | 0.0010 | 0.0010 | Ni | 0.0001 | 0.0001 | Mn | 0.0002 | 0.0001 |
| Co | 0.0005 | 0.0001 | P | 0.0011 | 0.0012 | W | 0.0015 | 0.0015 |
| Cr | 0.0002 | 0.0001 | Pb | 0.0008 | 0.0006 | Fe | 0.0018 | 0.0020 |
| Cu | 0.0005 | 0.0002 | Sn | 0.0019 | 0.0020 | Si | 0.0015 | 0.0015 |

From Table 2, the method has a lower background equivalent concentration, 0.0001% - 0.0019%, ie 5 ~ 95μg / L, between a small impact on the test results, indicating that through matrix matching and the synchronization background correction measures to eliminate the reagent and vanadium , aluminum body effects. Element detection limit of 0.0001% - 0.0020% that is 5.0 ~ 100μg / L, fully satisfy the need for detection of trace elements, including the requirement B ≤ 0.003, W ≤ 0.015 and other German GfE company standards.

### *3.3. The precision*

Choose a vanadium-aluminum alloy sample of 50 and 80 types, each sample was respectively digested and determined of eight independent. According to results of measurement 8 times, calculating the relative standard deviation as precision of the method, in which the relative standard deviation calculated by the formula: $RSD=\frac{\sqrt{\sum (x_i-\bar{x})^2}}{\frac{n-1}{\bar{x}}}\times 100\ \%$ .Shown in Table 3.

Table 3. The method accuracy experiments (n=8)

| Element | 50 type vanadium-aluminum alloy sample 1 | | | 80 type vanadium-aluminum alloy sample 2 | | |
|---|---|---|---|---|---|---|
| | Average(W/%) | Standard deviation(W/%) | RSD(%) | Average(W/%) | Standard deviation(W/%) | RSD(%) |
| As | 0.0136 | 0.0003 | 2.56 | 0.0009 | 0.0001 | 8.63 |
| B | 0.0004 | 0.0000 | 12.34 | 0.0017 | 0.0002 | 8.89 |
| Co | 0.0008 | 0.0001 | 7.13 | 0.0008 | 0.0001 | 13.36 |
| Cr | 0.0004 | 0.0000 | 12.34 | 0.0026 | 0.0001 | 3.79 |
| Cu | 0.0021 | 0.0001 | 5.14 | 0.0055 | 0.0002 | 4.31 |
| Fe | 0.0800 | 0.0016 | 1.99 | 0.176 | 0.0068 | 3.86 |
| Mg | 0.0004 | 0.0000 | 12.34 | 0.0046 | 0.0005 | 8.41 |
| Mn | 0.0117 | 0.0002 | 1.98 | 0.0148 | 0.0005 | 3.37 |
| Mo | 0.0047 | 0.0001 | 2.89 | 0.0046 | 0.0001 | 1.81 |
| Ni | 0.0003 | 0.0000 | 14.24 | 0.0023 | 0.0000 | 2.03 |
| P | 0.0008 | 0.0001 | 8.14 | 0.0030 | 0.0001 | 3.77 |
| Pb | 0.0012 | 0.0001 | 8.35 | 0.0016 | 0.0001 | 7.95 |
| Sn | 0.0012 | 0.0001 | 6.40 | 0.0001 | 0.0001 | 106.90 |
| Si | 0.0410 | 0.0020 | 4.88 | 0.0984 | 0.0011 | 1.13 |
| W | 0.0007 | 0.0001 | 13.23 | 0.0008 | 0.0001 | 10.60 |

Table 3 shows: in the range 0.010% - 0.200%, RSD ≤ 4.88%; within 0.001% to 0.010%, RSD ≤ 8.89%. Show that the method is highly feasible, better precision and reproducibility, to meet the determination need for micro or trace impurities in the vanadium-aluminum alloy.

### *3.4. The recover*

To test the accuracy of the results was determined, using the actual vanadium- aluminum alloy sample to be spiked recovery test, the recovery rate is calculated by the formula: Recovery rate= (Found after add standard - Found before add standard)÷Added×100%. Shown in Table 4.

Table 4 .Recoveries test (w/%)

| Element | 50 type vanadium-aluminum alloy sample 2 | | | | 80 type vanadium-aluminum alloy sample 2 | | | |
|---|---|---|---|---|---|---|---|---|
| | Found before add standard | Added | Found after add standard | Recovery | Found before add standard | Added | Found after add standard | Recovery |
| As | 0.0009 | 0.0120 | 0.0125 | 96.67 | 0.0008 | 0.0600 | 0.0598 | 98.33 |
| B | 0.0015 | 0.0040 | 0.0059 | 110.00 | 0.0008 | 0.0200 | 0.0211 | 101.50 |
| Co | 0.0007 | 0.0120 | 0.0137 | 108.33 | 0.0000 | 0.0600 | 0.0636 | 106.00 |
| Cr | 0.0008 | 0.0120 | 0.0139 | 109.17 | 0.0033 | 0.0600 | 0.0671 | 106.33 |
| Cu | 0.0020 | 0.0120 | 0.0144 | 103.33 | 0.0019 | 0.0600 | 0.0645 | 104.33 |
| Fe | 0.0717 | 0.0200 | 0.0910 | 96.50 | 0.3165 | 0.1000 | 0.4152 | 98.70 |
| Mg | 0.0008 | 0.0120 | 0.0128 | 100.00 | 0.0035 | 0.0600 | 0.0615 | 96.67 |
| Mn | 0.0081 | 0.0120 | 0.0204 | 102.50 | 0.0146 | 0.0600 | 0.0783 | 106.17 |
| Mo | 0.0049 | 0.0120 | 0.0174 | 104.17 | 0.0093 | 0.0600 | 0.0721 | 104.67 |
| Ni | 0.0003 | 0.0120 | 0.0134 | 109.17 | 0.0006 | 0.0600 | 0.0644 | 106.33 |
| P | 0.0012 | 0.0120 | 0.0127 | 95.83 | 0.0025 | 0.0600 | 0.0616 | 98.50 |
| Pb | 0.0008 | 0.0120 | 0.0127 | 99.17 | 0.0009 | 0.0600 | 0.0631 | 103.67 |
| Sn | 0.0001 | 0.0120 | 0.0130 | 107.50 | 0.0003 | 0.0600 | 0.0639 | 106.00 |
| Si | 0.0482 | 0.0200 | 0.0700 | 109.00 | 0.1943 | 0.1000 | 0.2896 | 95.30 |
| W | 0.0018 | 0.0120 | 0.0134 | 96.67 | 0.0009 | 0.0600 | 0.0640 | 105.17 |

The Table 4 shows the method to detect the elements recoveries were 95.3 ~ 110.0%, indicating the method is reliable and accurate.

### *3.5. Analysis of controlled trials*

Because in the absence of vanadium-aluminum alloy standard sample, we select the two 80 type vanadium-iron alloy European standard sample for testing the accuracy of the authentication method. Shown in Table 4.

Table 5.Analysis result comparison (%)

| Element | 591-1 | | SL25-07 | |
|---|---|---|---|---|
| | Found | Reference | Found | Reference |
| As | 0.0024 | 0.0022 | / | / |
| Co | / | / | 0.0095 | 0.009 |
| Cu | 0.0623 | 0.0596 | 0.0567 | 0.059 |
| Fe | 14.62 | 14.59 | 15.79 | 15.82 |
| Mn | 0.308 | 0.307 | 0.100 | 0.101 |
| Mo | / | / | 0.0162 | 0.015 |
| Ni | 0.0143 | 0.0141 | 0.0318 | 0.032 |
| P | 0.0289 | 0.0299 | 0.0295 | 0.031 |
| Si | 0.866 | 0.847 | 0.959 | 0.959 |
| W | / | / | 0.0292 | 0.029 |
| Ti | / | / | 0.049 | 0.047 |

Table "/" indicates that the element uncertain value.

Table 5 shows the results of the 80 type vanadium-iron alloy standard sample was determined consistent with the standard value.

At the same time, Germany GfE company, which is the world-class manufacturer of the vanadium-aluminium alloy, compared with this method into the test results, shown in Table 6.

Table 6.Analysis result comparison (%)

| element | measured value of this paper | Germany GfE | element | measured value of this paper | Germany GfE |
|---|---|---|---|---|---|
| Fe | 0.120 | 0.110 | Si | 0.101 | 0.092 |
| B | 0.0018 | 0.001 | P | 0.0016 | 0.002 |
| Mo | 0.0047 | 0.004 | Cr | 0.0025 | 0.002 |
| Cu | 0.0012 | 0.001 | W | 0.0035 | 0.003 |
| Mn | 0.0058 | 0.005 | Ni | 0.0019 | 0.002 |

Table 6 shows that this method and the German GfE company results were consistent.

## 3. Conclusion

Simultaneous directly determination of 15 kind of micro or the trace impurity elements in the Vanadium-aluminum alloy by ICP-AES, include boron, tungsten, silicon, iron, lead, tin, arsenic, nickel, chromium, cobalt, copper, phosphorus, manganese, magnesium and the molybdenum. Studied the matrix vanadium, aluminum and between coexisting elements impact analysis of spectral lines, by optimizing the background correction and other measures to avoid spectral interferences. Method is simple and easy to operate, and less interference factors such as background and matrix effects, the detection limit and background equivalent concentration is low, multi-element detection, content range, good precision, high accuracy. To meet the German GfE's technical standards, and comply with high levels of aerospace grade vanadium-aluminum alloy product products inspection requirements

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